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(56) References Cited:

DE	196 09 419 A1
EP	07 07 957 A1
EP	02 29 715 A1
WO	98 32 786 A1
WO	96 07 699 A1
JP	58-14 550 A

The following information was taken from documents filed by Applicant
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(54) **Elastic Fibers, Films, Textile Fabrics and Hybrid Structures with High Low-Temperature Shrinkability and High Heat Stability, Process for Making Same and Use Thereof**

(57) The invention relates to the fields of chemistry [and textile technology] and concerns elastic fibers etc used for the packaging of goods.

The object of the invention is to attain high shrinkage of elastic fibers etc already at low temperatures.

This objective is reached by use of elastic fibers etc obtained by graft-copolymerizing with an organosilane at least two polyethylene/octene copolymers with a molecular weight M_w ranging from 40,000 to 180,000 g/mol and an imparted orientation.

Moreover, said objective is reached by use of a process for making elastic fibers etc. according to Claim 1 whereby a mixture is prepared from at least two polyethylene/octene copolymers, to which mixture grafting and crosslinking agents are added before and/or during the mixing. The resulting mixture is then processed thermoplastically and shaped, followed by storage under shape-setting conditions.

SPECIFICATION

The invention relates to the fields of chemistry and textile technology and to the packaging sector and concerns elastic fibers, films, textile fabrics and hybrid structures such as those used for the packaging of goods and for achieving special textile effects, for example, hybrid bulked fiber structures. The invention also relates to a process for making such products and to the use thereof.

In industrial shaping, the acting forces stretch polymeric materials in the entropy-elastic state. The macromolecules are thus partly uncoiled and deformed and are given a more or less pronounced preferential orientation which depends on the deformation stress and which is associated with an anisotropy of physical properties.

From the tendency of the partly uncoiled and deformed macromolecule to assume the energetically most favorable state, namely the thermodynamic state of the highest possible entropy (i.e., maximum disorder), it follows that when a higher temperature is reached, in the entropy-elastic state, a latent recovery force is activated in the elastic fibers, films, textile fabrics and hybrid structures made therefrom. Shrinkage ensues and, for example in the packaging industry, is used intentionally for a specific purpose. Also, in the production of man-made fibers, different shrinkage tendencies of two differently structured polymeric materials are utilized in bilateral fiber structures to achieve self-curling or splitting of the fibers.

In DE 196 09 419 A1 are described melt-spun crosslinked elastic fibers of a special polyethylene and a process for their production and use. They have the drawback that they are limited to polyethylene with a defined side chain structure and a narrow molecular weight distribution $M_w/M_n < 2.2$ which does not permit control of material parameters within wider limits. Moreover, to reduce the viscosity, it is recommended to incorporate plasticizer oils. The attendant significant reduction in gel content and degree of crosslinking cause deterioration of mechanical, thermal and mechanical properties.

JP 58-214550 A 2 describes synthetic fabrics which can be made to shrink even at low temperatures. Synthetic fibers which have been melt-spun separately from a propylene - α -olefin copolymer or from a mixture of the copolymer and polypropylene develop their high shrinkage, induced by heat treatment, only at about 100 °C and can serve as starting materials for the preparation of shrink fabrics for packaging purposes. Another drawback of this mixture lies in its low heat resistance (< 100 °C) after the second heating required to bring about shrinkage.

EP 707957 A1 describes a multilayer film based on an ethylene - α -olefin copolymer. Differential scanning calorimetry [DSC] showed the main melting peak of the ethylene - α -olefin copolymer to be below a temperature of 105 °C and to exhibit free shrinkage of at least 80% at 85 °C. The other layers of the multilayer film are shrink-compatible and optionally consists of other polymers, for example of the crosslinked Affinity PF 1140 or irradiated ethylene - vinyl acetate [EVA]. In this case, too, the drawback lies in the high shrink temperature.

EP 229 715 A2 also discloses a multilayer film which presents high shrinkage but only weak shrinkage forces. The film consist of one or two outer layers of polyethylene, polypropylene and/or ethylene-propylene copolymer and a core layer of polyethylene which has a lower melting point than the outer layers. A film constructed in this manner, because of previously imparted orientation, shows at 60 °C a shrinkage of 2.5%, at 80 °C one of 16.5%, at 100 °C one of 29.5% and at 120 °C one of 45%. Here, too, the drawback lies in the relatively high shrink temperature, the expensive processing technology (coextrusion), the low heat resistance (< 100 °C after the second heating and the low maximum shrinkage of 45%.

WO 96/07699 discloses a biaxially oriented copolymer film consisting of a polyolefin copolymer, a polyolefin terpolymer and the possible blends with, among others, homopolymeric polyolefins. The film exhibits high shrinkage, it being possible to adjust shrinkage in the machine and cross directions in controlled fashion.

Here, too, the drawback lies in the high shrink temperatures of 100-140 °C.

Also known are stretch films of metallocene-catalyzed polyethylene. Compared to the conventional polyethylene [PE] products, they exhibit advantages in preparation and quality. "They can be prestretched to a higher degree which results in higher mechanical strength and the possibility of obtaining thinner films" [according to N. Rose, P. Bailey and S. Ohlsen, *Kunststoffe* 87, 1374-1378 (1997)].

Another possibility of using shrinkability intentionally lies in the preparation of hybrid fiber structures for the textile industry. Two different polymers are made into a bonded filament by simultaneous processing (coextrusion, bicomponent spinning, elementary fiber blending). Heating then causes differential shrinking which leads to bulking, curling or splitting of the filaments or of the textile fabric. This effect can be utilized, for example, in the production of microfibers with a high specific surface such as those used in numerous industrial filters and nonwoven fabrics.

Bicomponent fibers and nonwoven fabrics in which the desired splitting or curling occurs even at low temperatures ($T < 80$ °C) as a result of differential shrinkage are currently not known.

Also unknown are elastic fibers, films, textile fabrics and hybrid structures in which high shrinkage ($S > 30\%$) can be brought about already at low temperatures ($T < 80$ °C).

The object of the invention is to obtain in elastic fibers, films, textile fabrics and hybrid structures with high shrinkage ($S > 30\%$) even at low temperatures ($T < 80$ °C) and to achieve dimensional stability and elasticity by further heating or reheating far above the shrink temperature ($T > 140$ °C).

This objective is reached according to the invention as disclosed in the claims. Other embodiments of the invention are described in the subclaims.

According to the invention, first a blend consisting of at least two polyethylene/octene copolymers with molecular weights ranging from 40,000 to 180,000 g/mol are prepared and melted. This blend is rendered crosslinkable by peroxide-initiated organosilane grafting onto the polyethylene main chain and/or side chains. This step occurs with thermal decomposition of the peroxide and subsequent action of the resulting free radicals upon the polyethylene main chain and/or side chains which gives rise to hydrogen abstraction. The vinyl group in the organosilane opens, followed by covalent coupling of the organosilane to the polyethylene main chain and/or side chains. By thermoplastic processing, the melt is shaped to give elastic fibers, films, textile fabrics or hybrid structures. During thermoplastic shaping of the functionalized blend, uniaxial stretching deformation in the course of melt-spinning and a uniaxial or biaxial stretching deformation in the course of film production impart orientations which are essentially irreversible. Orientation can also be imparted totally or partially in a subsequent processing step. The cooling time available in the shaping process until the melt solidifies is shorter than the relaxation time of the blend. A covalent network is formed in the solid state with shape-setting brought about by a hydrolytic and condensation reaction of the grafted-on organosilanes via Si-O-Si bridges. The crosslinking reactions whereby the material obtains its heat resistance can be accelerated by use of a catalyst. The elasticity obtained by crosslinking compared to that in the non-crosslinked state is characterized by higher recovery forces and a lower permanent deformation. In the crosslinked state, the material continues to be shrinkable.

Surprisingly, we have now found that despite a higher polydispersity caused by blending, a more stable, largely fiber-breakage-free melt-spinning process is possible at the usual high-speed spinning rates (2000-4000 m/min). We have also found that the viscosity of the functionalized blend can be adjusted within a wide range by use of appropriate base polymer types. Organosilane graft copolymerization raises the melt viscosity. The instability during spinning that is normally observed as a result of this can be preventively

reduced by increasing the amount of low-molecular-weight polymer in the blend. Surprisingly, the blending of at least two starting polymers also brings about synergistic effects in the mechanical properties of the blend. Thus, we have surprisingly found that the tensile strength (highest tensile strength in the stress - elongation curve, based on the initial fineness) and the elongation at the highest tensile stress of a blend increase despite the lower molecular weight compared to the unblended starting polymer with the highest molecular weight, and this also has a positive effect on the stability of the shaping process.

The amount of peroxide used requires special attention because of the effect of its active oxygen. An excessive amount of added peroxide can start crosslinking or bring about premature crosslinking which makes it impossible to carry out flawless thermoplastic shaping. If, on the other hand, the amount of added peroxide is not sufficient, the gel content and the crosslink density may decrease. An increasing amount of peroxide causes primarily a significant increase in melt viscosity which has a deleterious effect on thermoplastic processability.

It is also advantageous to add during or after the functionalization of the blend from 0.01 to 2 parts per hundred [phr] and preferably from 0.05 to 1.2 phr of a vinyl monomer. Particularly advantageous is the doping with monomeric styrene. Thus, we have surprisingly found that the addition of the vinyl monomer not only advantageously modifies the rheological properties of the grafted ethylene-octene copolymer blend, but that the mechanical properties of both the grafted and the crosslinked blend are clearly improved and that the stability of the thermoplastic shaping process is increased at the same time. The thermal stability of the crosslinked blend can be intentionally adjusted by controlled feeding of the added vinyl monomer which more or less reduces the gel content and the crosslink density.

We found that to obtain a shaped product with good mechanical and thermal properties it was particularly advantageous to carry out the entire process of blending the starting polymers, their subsequent functionalization with organosilanes, the addition of peroxide and the shaping in a one-step extrusion process, advantageously by means of a twin-screw extruder.

To obtain hybrid structures, it is also advantageous to process the elastic fibers, films or textile fabrics of the invention with fibers, films or textile fabrics made of other materials used for producing fibers or fabrics.

During the shaping of the functionalized blend to obtain elastic fibers, films, textile fabrics and hybrid structures, uniaxial or biaxial stretching imparts an orientation before these products are wound up in shape-setting manner. As is known, this results in a large proportion of irreversible orientations. These irreversible orientations can also be imparted in a subsequent stretching process which either follows the shaping process directly on-line (for example in the form of a stretch-spinning process during filament production) or involves an additional filament processing step off-line (for example, draw-twisting, draw-texturing or draw warping).

In melt-spinning, a water-based spinning preparation is applied after filament formation. Said preparation is intended, among other things, to bring about a significant reduction in the coefficient of friction between the filaments and the filament guides during further filament processing and to initiate crosslinking via -O-Si-O- bridges by a hydrolytic and condensation reaction.

To accelerate the hydrolytic and condensation reaction, it is advantageous to add to the melt a catalyst, for example dibutyltin dilaurate (DBTL) in an amount of ≤ 0.04 phr. It is also possible to add a catalyst, for example dibutyltin dilaurate (DBTL) to the aqueous spinning preparation in an amount of ≤ 3 wt%.

Moreover, the following advantages can be achieved by the solution provided by the invention:

The marked stickiness normally exhibited by the elastomeric polyethylene/octene copolymer is eliminated.

Moreover, by varying numerous formulation-dependent and process-dependent parameters

(for example, the silane content, silane type, blending ratio, type and concentration of the vinyl monomer, draw-off speed, stretching ratio, temperature program), it is possible to "construct" a fiber, a textile fabric and a hybrid structure so as to obtain a desired property profile in terms of heat stability, shrinkage adjustable in a defined manner, pronounced elasticity in the stress-elongation behavior, weldability and sealability as well as recyclability.

Moreover, as a result of the solution provided by the invention, it is possible to control the viscosity of the melt. This can be achieved by varying the mixing ratio of the starting polymers of different molecular weights. The higher the proportion of ethylene-octene copolymer of low molecular weight, the lower is the resulting viscosity of both the grafted and the nongrafted blend.

The solution of the invention also provides control of the irreversible orientations which are responsible for the degree of shrinkage. In melt spinning, the extent of the irreversible orientation of the polymer molecules along the fiber axis is essentially determined by the spinning rate.

In film blowing, two mutually independent stretching rates are applied in radial and axial film tube direction up to the solidification of the melt. In this manner, the thermoplastic melt undergoes nonhomogeneous, nonuniform, biaxial stretching which is primarily responsible for the imparted orientations. In all cases, the relaxation times of the grafted blends will not exceed the cooling time available for the process.

To achieve the required shape setting, the take-up bodies (spinning bobbin, core of the film reel) which are available in any case, can be used for the products made.

In the following, the invention will be illustrated by way of several practical examples.

EXAMPLE 1

Starting Materials:

1. 100 phr of a mixture of 50 wt% of polyethylene/octene copolymer Engage 8200 and 50 wt% of polyethylene/octene Engage 8400,
2. 1.5 phr of vinyltrimethoxysilane (VTMOS),
3. 0.043 phr of 2,5-dimethylhexane-2,5-dibutyl peroxide (DHBP).

The granular Engage materials were mixed with the other starting materials in an extruder and then melted. This resulted in peroxide-initiated organosilane grafting. The functionalized melt was then transferred to the melt spinning unit. The parameters of the reactive extrusion and of the melt spinning were as follows:

Temperatures of extruder heating zones 1 - 7: 235 °C
 Extruder screw speed: 160 rpm
 Melt temperature: 239 °C
 Spinning head temperature: 245 °C
 Extrusion pressure: 3.5 MPa
 Spinneret: 12-hole, hole diameter 0.45 mm, hole length 0.9 mm,
 Total spinneret throughput (12 filaments): 17.9 g/min
 Blow air temperature: 15.7 °C,
 Blow air velocity: 0.35 m/s,
 Relative humidity of blow air: 60%.

The melt was extruded through the spinneret at a constant rate by means of a spinning pump located after the extruder, drawn off from the spinneret at a speed produced by a system of godet rollers and wound on a bobbin at an only slightly different speed. After the filaments had solidified and before the spinning speed was imparted by the system of godet rollers, a water-containing spinning preparation was applied to the filaments by a treatment system thus starting the structure-crosslinking hydrolytic and condensation reaction. The wind-up speed was 500 m/min.

After filament winding, the filaments in fixed shape on the bobbin were subjected to crosslinking by applying to the wound bobbin an isopropanol - water mixture containing 1 wt% of DBTL.

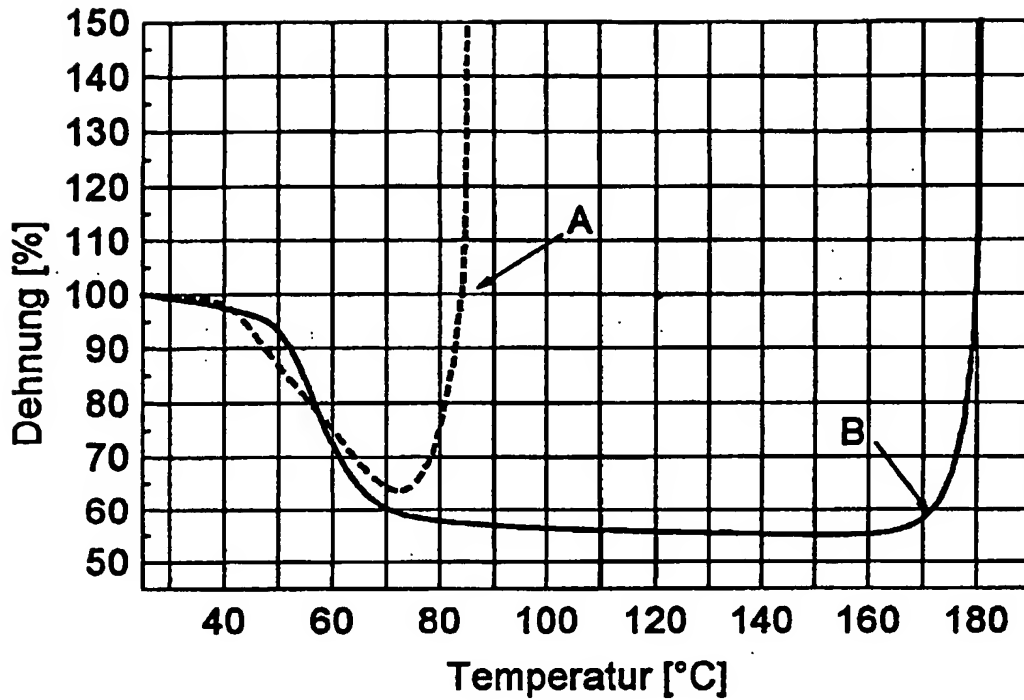
The gel content was determined after 16 h of boiling in xylene. The solid phase shrinkage was measured on filament bundles after these were taken off the bobbins and stored in the unstrained state 96 h under standard conditions (20 °C, 65% rel. humidity).

The following filament properties were obtained:

Tensile strength R_H : 0.205 cN/dtex
 Elongation at maximum tensile stress Δ_H : 272.33%
 Solid phase shrinkage: 5.5%
 Shrinkage by thermomechanical analysis [TMA]: > 40%
 Gel content: 73%

Fig. 1 shows the behavior of filaments A and B under thermomechanical stress (TMA) (TMA parameters: heating rate 10 K/min, pretension 0.025 cN/tex).
 Filament A; spun filament of ungrafted polyethylene/octene copolymer,
 Filament B: filament according to the invention.

Fig. 1



"Temperatur" = Temperature; "Dehnung" = Elongation

EXAMPLE 2

The starting materials and the preparation of the elastic filaments therefrom were the same as in Example 1, but the spinning and wind-up velocity was 2000 m/min.

After the crosslinking, filament properties were determined as in Example 1, with the following results:

Tensile strength R_H : 0.356 cN/dtex

Elongation at maximum tensile stress \dot{a}_H : 127.55%

Solid phase shrinkage: 14.3%

Shrinkage by TMA: > 66%

Gel content: 69.5%

The crosslinked filaments were thermally stable up to about 160 °C, as shown in Fig. 1.

EXAMPLE 3

Starting materials:

1. 100 phr of a mixture of 50 wt% of polyethylene/octene copolymer Engage 8200 and 50 wt% of polyethylene/octene Engage 8400,
2. 3 phr of vinyltrimethoxysilane (VTMOS),
3. 0.086 phr of 2,5-dimethylhexane-2,5-dibutyl peroxide (DHBP),
4. 0.12 phr of monomeric styrene.

The preparation of the elastic filaments from the starting materials was as in Example 1, but the spinning and wind-up velocity was 500 m/min.

Filament properties were determined as in Example 1 before and after crosslinking, with the following results.

In the grafted, uncrosslinked state:

Tensile strength R_H : 0.219 cN/dtex

Elongation at maximum tensile stress \dot{a}_H : 613%.

In the crosslinked state:

Tensile strength R_H : 0.309 cN/dtex

Elongation at maximum tensile stress \dot{a}_H : 601%.

Solid phase shrinkage: 5.5%,

Shrinkage by TMA > 56%

Gel content: 56%.

At this point, note once again the increase in the strength of filaments obtained from the grafted blend when they are crosslinked by addition of styrene. The property gain is indicated by an increase in tensile strength of 29% ($R_H = 0.219$ cN/dtex $\rightarrow R_H = 0.309$ cN/dtex) whereas the elongation at maximum tensile stress shows hardly any change ($\dot{a}_H = 613\%$ $\rightarrow \dot{a}_H = 601\%$). The shrinkage behavior is similar to that shown in Fig. 1, the filaments being thermally stable up to at least 140 °C.

PATENT CLAIMS

1. Elastic fibers, films, textile fabrics and hybrid structures with high shrinkability at low temperatures and high heat stability obtained by graft-copolymerizing with an organosilane at least two polyethylene/octene copolymers having a molecular weight M_w from 40,000 to 180,000 g/mol and an imparted orientation and which are crosslinked via Si-O-Si bridges by hydrolytic and condensation reactions.
2. Elastic fibers, films, textile fabrics and hybrid structures according to Claim 1, in which the molecular weights M_w range from 50,000 to 170,000 g/mol.
3. Process for making elastic fibers, films, textile fabrics and hybrid structures with high shrinkability at low temperatures and with high heat stability as in Claim 1, whereby a mixture is prepared from at least two polyethylene/octene copolymers to which mixture grafting and crosslinking agents are added before and/or during the mixing, the resulting functionalized mixture being processed thermoplastically, the shaping then being carried out during which molecular orientations are imparted to the elastic fibers, films, textile fabrics and hybrid structures, followed by storage to set the shape during which crosslinking essentially takes place.
4. Process according to Claim 3, whereby different polyethylene/octene copolymers are used.
5. Process according to Claim 4, whereby a polyethylene/octene copolymer with a molecular weight $M_w = 90,000$ g/mol (Engage 8200) and/or a polyethylene/octene copolymer with a molecular weight $M_w = 72,900$ g/mol (Engage 8411) and/or a polyethylene/octene copolymer with a molecular weight $M_w = 48,000$ g/mol (Engage 8400) and/or a polyethylene/octene copolymer with a molecular weight $M_w = 46,000$ g/mol (Engage 8401) is used.
6. Process according to Claim 3, whereby two polyethylene/octene copolymers are used in an amount ranging from 35-65 wt% to 65-35 wt%.
7. Process according to Claim 3, whereby 0.01 to 2 phr of a vinyl monomer is added.
8. Process according to Claim 7, whereby 0.01 to 2 phr of monomeric styrene is added.
9. Process according to Claim 3, whereby the control of viscosity is accomplished by varying the mixing ratio of the starting materials of different molecular weights, viscosity decreasing with lower molecular weights.
10. Process according to Claim 3, whereby the control of the imparted molecular orientations is accomplished by varying the stretching ratio, a higher stretching ratio producing a higher molecular orientation of the material
11. Process according to Claim 3, whereby a catalyst is added to the melt in an amount of ≤ 0.04 phr.
12. Process according to Claim 3, whereby the crosslinking of the functionalized materials is initiated with a water-containing spinning preparation.
13. Process according to Claim 3, whereby a catalyst in an amount of ≤ 3 wt.% is added to accelerate the crosslinking induced by the water-containing preparation.

14. Process according to Claim 11 or 13, whereby dibutyltin dilaurate is added as catalyst.
15. Process according to Claim 3, whereby the mixture of starting materials with or without other added substances and the thermoplastic processing of said mixture are carried out in a single processing step.
16. Process according to Claim 15, whereby the single processing step process is carried out in a twin-screw extruder.
17. Process according to Claim 3, whereby to obtain a hybrid structure the elastic fibers, films or textile fabrics are processed with fibers, films or textile fabrics made from other materials used to make fibers or fabrics.